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EP-A- 0 166 611  
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JP-A-56 099 401 (KUMIAI CHEM. IND. K.K.)  
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WPIL, FILE SUPPLIER, AN=84-149101 (24),  
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(73) Proprietor : SOMAR CORPORATION  
11-2, Ginza 4-chome Chuo-ku  
Tokyo 104 (JP)

(72) Inventor : Funatsu, Ryoji  
Azusaen 203, 13-7 Nishiari 3-chome  
Adachi-ku, Tokyo (JP)  
Inventor : Kurose, Shigeru  
3-10-6-4-3, Hikonari  
Misato-shi, Saitama-ken (JP)  
Inventor : Mitsui, Susumu  
Charme-Kitakoshigaya B-303, 1006-3  
Ofusa Koshigaya-shi, Saitama-ken (JP)  
Inventor : Goto, Atsuko  
Sasai Mansion 304, 3-17-9, Osawa  
Koshigaya-shi, Saitama-ken (JP)

(74) Representative : Allam, Peter Clark et al  
LLOYD WISE, TREGEAR & CO. Norman House  
105-109 Strand  
London WC2R 0AE (GB)

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**Description**

This invention relates generally to a germicide suitable for preventing growth of various germs such as yeasts and filamentous fungi in industrial water such as waste water from pulp mills or cooling water for heat exchangers and, more specifically, to a germicidal composition of the above-mentioned type which is stable and has an improved shelf life.

In industrial water such as waste water from paper making steps in pulp-related industries and recirculating cooling water used in various mills, microorganisms such as germs, fungi and bacteria are apt to grow to form slimes which cause various problems. To cope with this, various germicides have been proposed and some of them are actually used for destroying germs or preventing growth of germs in various fields. Among various germicides, an isothiazolone compound is known to be especially effective in preventing the occurrence of slimes. Isothiazolone compound-containing germicides are generally stored, transported or placed on sales in the form of concentrated solutions. Glycols, ketones or ethers are generally used as solvents for such germicidal solutions.

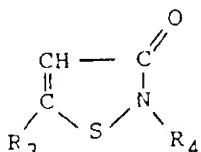
It has been found, however, that isothiazolone compounds in such solutions are not stable and, therefore, the germicidal activity of such solutions is gradually degraded when stored for a long period of time.

The present invention has been made with the above problem of the conventional germicides in view and is contemplated to provide an isothiazolone-type germicide having an improved shelf life. In accordance with the present invention there is provided a composition in the form of a solution, comprising:

- 20      an isothiazolone compound; and
- a solvent containing at least 50 % by weight of 3-methyl-3-methoxybutyl alcohol.

Any isothiazolone compound may be used for the purpose of the present invention as long as it has a germicidal activity. If desired, a mixture of two or more isothiazolone compounds may be used. Particularly suited are isothiazolone compounds represented by the following general formula:

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wherein R<sub>3</sub> stands for hydrogen or halogen and R<sub>4</sub> stands for hydrogen or alkyl. Illustrative of suitable isothiazolone compounds are 2-methyl-3-isothiazolone, 5-chloro-2-methyl-3-isothiazolone, 2-octyl-3-isothiazolone, 2-ethyl-3-isothiazolone and mixtures thereof. Complexes of isothiazolones, such as calcium chloride complexes, magnesium nitrate complexes and iron chloride complexes, may also be used, though the use of free form isothiazolones is preferred.

The present invention is characterized by using 3-methyl-3-methoxybutyl alcohol as a stabilizing liquid which constitutes the major component of a solvent for the isothiazolone compound. It is important that the solvent should comprise at least 50 % by weight, preferably at least 60 % by weight of the stabilizing liquid in order to attain the object of the present invention.

If desired, an auxiliary organic solvent may be used in conjunction with the stabilizing liquid. Examples of such auxiliary solvents include monohydric alcohols such as benzyl alcohol, butanol and isopropyl alcohol; glycols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol and propylene glycol; ethers such as ethylene glycol mono(or di)alkyl ether, 1,4-dioxane, dibenzyl ether and propylene oxide; esters such as ethylene glycol monoacetate, alkyl acetates and alkyl adipates; hydrocarbons such as dodecylbenzene and pseudocumene, amides such as dimethylformamide; ketones such as methyl isobutyl ketone; and dimethylsulfoxide. The amount of such an auxiliary solvent should not exceed 50 % by weight of the solvent.

The solvent, comprising the above stabilizing liquid and, optionally, the above auxiliary solvent, is generally used in an amount so that the concentration of the isothiazolone compound is 0.1-70 % by weight, preferably 0.4-50 % by weight, based on the total weight of the isothiazolone compound and the solvent.

If desired, isothiazolone compounds may be used in conjunction with one or more other germicides such as 4,5-dichloro-1,2-dithiole-3-one, 2,2-dibromo-3-nitrilepropionamide, 2,2-dibromo-2-nitroethanol, methylenebis thiocyanate, 1-chlorobenzaldioxime acetate and bis(bromoacetoxy)butene.

Solutions of an isothiazolone compound in the above solvent comprising stabilizing liquid are excellent in stability and the isothiazolone compound in the solution is prevented from decomposing for a long period of time. Thus, degradation of germicidal activity during storage or transportation is effectively prevented, so that the solution is advantageously used as a germicide or a raw material for the production of germicides.

The following examples will further illustrate the present invention.

Examples 1-17

5 One or more of the isothiazolone compounds shown in Table 1 were dissolved in 3-methyl-3-methoxybutyl alcohol of the formula:  $\text{CH}_3\text{O} - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$  or a mixed solvent composed of 3-methyl-3-methoxybutyl alcohol and the auxiliary solvent shown in Table 1. The amounts (parts by weight) of the isothiazolone compounds, 3-methyl-3-methoxybutyl alcohol and the auxiliary solvents are also shown in Table 1.

10 In Table 1, the abbreviations are as follows:

Isothiazolone Compound:

15 ITZ-1: 5-Chloro-2-methylisothiazolone  
 ITZ-2: 2-Methylisothiazolone  
 ITZ-3: 2-Octylisothiazolone

Stabilizing Liquid:

20 MMB: 3-Methyl-3-methoxybutyl alcohol

Auxiliary Solvent:

25 EG: Ethylene glycol  
 DEG: Diethylene glycol  
 PG: Propylene glycol  
 DGME: Diethylene glycol monomethyl ether  
 MBK: Methyl isobutyl ketone  
 DBE: Dibenzyl ether  
 30 PO: Propylene oxide  
 PEG: Polyethylene glycol (molecular weight: 400)

The thus prepared solutions were then allowed to stand at 40 °C for 30 days. The concentration (C) of the isothiazolone compound or compounds in each solution was measured 5, 10, 20 and 30 days after the preparation thereof to evaluate the stability thereof in terms of "survival rate" calculated from the following equation:

$$35 \quad \text{Survival rate} = \frac{C}{C_0} \times 100 \%$$

wherein C represents the measured concentration and  $C_0$  represents the initial concentration. The results are also shown in Table 1.

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Table 1

Example No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Isothiazolone																	
ITZ-1	20				15	20	20	20	20	20	20	20	20	15	15	5	5
ITZ-2		20			5									5	5		
ITZ-3			20											5	20		
Stabilizing Liquid																	
NMB	80	80	80	80	50	50	50	50	50	50	50	50	50	50	50	70	95
Auxiliary Solvent																	
EG							30							30	10		35
DEG							30								10		
PG							30										
DGME																	
MBK																	
DBE																	
PO																	
PEG																	
Survival Rate (%)																	
5 days	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
10 days	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
20 days	100	100	100	100	98	98	95	98	93	96	98	98	98	100	100	100	99
30 days	99	100	100	100	95	96	92	96	88	91	96	97	98	98	100	100	98

Comparative Examples 1-17

The procedures of the above examples were repeated in the same manner as described except that the  
5 amounts of 3-methyl-3-methoxybutyl alcohol and the auxiliary solvents were changed as shown in Table 2.  
The results are also summarized in Table 2.

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Table 2

Comparative Example No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Isothiazolone																	
ITZ-1	20				15	20	20	20	20	20	20	20	15	15	5	5	5
ITZ-2		20			5								5	5			
ITZ-3			20										5	5	20		
Stabilizing Liquid																	
MMB																	
Auxiliary Solvent																	
EG	80	80															
DEG			80														
PG			80														
DGME				80													
NBK					80												
DBE						80											
PO							80										
PEG								80									
Survival Rate (%)																	
5 days	86	99	100	98	85	65	85	50	63	98	96	100	100	96	100	90	100
10 days	75	88	96	80	24	16	80	2	8	86	76	90	82	92	66	90	66
20 days	69	54	65	65	13	5	52	0	0	70	75	46	32	26	62	34	62
30 days	3	25	45	12	2	0	9	0	0	6	3	2	0	0	21	6	10

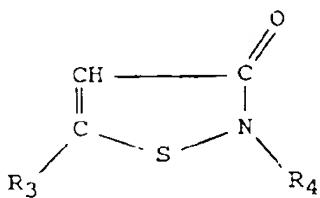
**Claims**

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1. A germicidal composition comprising:  
a solvent which comprises at least 50% by weight of 3-methyl-3-methoxybutyl alcohol, and  
an isothiazolone compound dissolved in said solvent
- 10 2. A composition according to Claim 1, wherein the isothiazolone compound is present in an amount of 0.1-70% by weight.
- 15 3. A composition according to Claim 1 or Claim 2, wherein said isothiazolone compound is at least one compound selected from those represented by the following general formula:

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wherein R<sub>3</sub> stands for hydrogen or halogen and R<sub>4</sub> stands for hydrogen or alkyl, and complexes thereof.

4. A composition according to any preceding claim, wherein the content of said 3-methyl-3-methoxybutyl alcohol in said solvent is at least 60% by weight.
- 30 5. A composition according to any preceding claim, further comprising one or more germicide selected from the group consisting of 4,5-dichloro-1,2-dithiole-3-one, 2,2-dibromo-3-nitrilepropionamide, 2,2-dibromo-2-nitroethanol, methylenebisthiocyanate, 1-chlorobenzaldoxime acetate and bis(bromoacetoxy)butene.
- 35 6. A composition according to any preceding claim, wherein the solvent comprises one or more auxiliary organic solvents.

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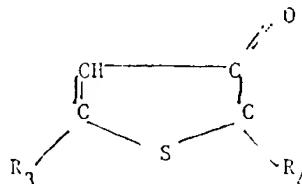
**Patentansprüche**

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1. Eine keimtötende Verbindung umfassend :  
ein Lösungsmittel mit mindestens 50 Gew.% 3-Methyl-3- Methoxybutylalkohol und  
eine in dem besagten Lösungsmittel aufgelöste Isothiazolonverbindung.
2. Eine Verbindung nach Anspruch 1, bei der die Isothiazolonverbindung in einer Menge von 0,1-70 Gew.% vorhanden ist.
- 45 3. Eine Verbindung nach Anspruch 1 oder Anspruch 2, bei der die besagte Isothiazolonverbindung mindestens eine Verbindung aus der der folgenden allgemeinen Formel

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entsprechenden Gruppe ist, wobei R<sub>3</sub> für Wasserstoff oder Halogen und R<sub>4</sub> für Wasserstoff oder Alkyl und Komplexe davon steht.

4. Eine Verbindung nach einem der vorstehenden Ansprüche, bei der der Anteil des besagten 3-Methyl-3-Methoxybutylalkohols in dem besagten Lösungsmittel mindestens 60 Gew.% beträgt.

5. 5. Eine Verbindung nach einem der vorstehenden Ansprüche, die des weiteren ein oder mehrere keimtötende Verbindungen aus der 4,5-Dichlor- 1,2-Dithiol-3-on, 2,2-Dibrom-3-Nitrilpropionamid, 2,2-Dibrom-2-Nitroäthanol, Methylenbisthiocyanat, 1-Chlorbenzaldoximacetat und Bis(Bromacetoxo)Buten umfassenden Gruppe enthält.

10. 6. Eine Verbindung nach einem der vorstehenden Ansprüche, bei der das Lösungsmittel ein oder mehr organische Zusatzlösungen umfaßt.

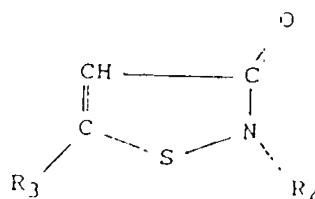
**Revendications**

15. 1. Composition germicide comprenant:  
un solvant contenant au moins 50% en poids d'alcool 3-méthyle-3-méthoxybutyl, et  
un composé d'isothiazolone dissous dans ledit solvant.

20. 2. Composition selon Revendication 1, dans laquelle le composé d'isothiazolone est présent en proportion de 0,1-70% en poids.

30. 3. Composition selon Revendication 1 ou Revendication 2, dans laquelle le composé d'isothiazolone est au moins un composé choisi entre ceux qui sont représentés par la formule générale:

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35. dans laquelle R<sub>3</sub> représente l'hydrogène ou un halogène et R<sub>4</sub> représente l'hydrogène ou un alkyle, et des composés de ces éléments.

40. 4. Composition selon l'une quelconque des revendications précédentes, où la teneur en alcool 3-méthyle-3-méthoxybutyl dudit solvant est d'au moins 60% en poids.

45. 5. Composition selon l'une quelconque des revendications précédentes, comprenant en outre un ou plusieurs germicides choisis dans le groupe comprenant le 4,5-dichloro-1,2-dithiol-3-one, le 2,2-dibromo-3-nitrilepropionamide, le 2,2-dibromo-2-nitroéthanol, le méthylénébisthiocyanate, l'acétate de 1-chlorobenzaldoxime et le bis(bromoacétoxy)butène.

50. 6. Composition selon l'une quelconque des revendications précédentes, dans laquelle le solvant comprend un ou plusieurs solvants organiques auxiliaires.

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